Supporting Information for

T-Shaped Push-Pull Chromophores: First Modification of the Indan-1,3-dione Fused Benzene Ring by Cross-Coupling Reactions

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1. $^1$H and $^{13}$C NMR spectra

**Figure S1** $^1$H NMR spectrum of compound 1 (400 MHz, CDCl$_3$, 25 °C).

**Figure S2** $^{13}$C APT NMR spectrum of compound 1 (100 MHz, CDCl$_3$, 25 °C).
**Figure S3** $^1$H NMR spectrum of compound 2 (400 MHz, CDCl$_3$, 25 °C).

**Figure S4** $^{13}$C APT NMR spectrum of compound 2 (100 MHz, CDCl$_3$, 25 °C).
Figure S5 $^1$H NMR spectrum of compound 3 (400 MHz, CDCl$_3$, 25 °C).

Figure S6 $^{13}$C APT NMR spectrum of compound 3 (100 MHz, CDCl$_3$, 25 °C).
Figure S7 $^1$H NMR spectrum of compound 4 (400 MHz, CDCl$_3$, 25 °C).

Figure S8 $^{13}$C APT NMR spectrum of compound 4 (100 MHz, CDCl$_3$, 25 °C).
Figure S9 $^1$H NMR spectrum of compound 5 (400 MHz, CDCl$_3$, 25 °C).

Figure S10 $^{13}$C APT NMR spectrum of compound 5 (100 MHz, CDCl$_3$, 25 °C).
Figure S11 $^1$H NMR spectrum of compound 6 (400 MHz, CDCl$_3$, 25 °C).

Figure S12 $^{13}$C APT NMR spectrum of compound 6 (100 MHz, CDCl$_3$, 25 °C).
Figure S13 $^1$H NMR spectrum of compound 7 (400 MHz, CDCl$_3$, 25 °C).

Figure S14 $^{13}$C APT NMR spectrum of compound 7 (100 MHz, CDCl$_3$, 25 °C).
Figure S15 $^1$H NMR spectrum of compound 8 (400 MHz, CDCl$_3$, 25 °C).

Figure S16 $^{13}$C APT NMR spectrum of compound 8 (100 MHz, CDCl$_3$, 25 °C).
Figure S17 $^1$H NMR spectrum of compound 9 (400 MHz, CDCl$_3$, 25 °C).

Figure S18 $^{13}$C APT NMR spectrum of compound 9 (100 MHz, CDCl$_3$, 25 °C).
Figure S19 $^1$H NMR spectrum of compound 10 (400 MHz, CDCl₃, 25 °C).

Figure S20 $^{13}$C APT NMR spectrum of compound 9 (100 MHz, CDCl₃, 25 °C).
Figure S21 $^1$H NMR spectrum of compound 11 (400 MHz, CDCl$_3$, 25 °C).

Figure S22 $^{13}$C APT NMR spectrum of compound 11 (100 MHz, CDCl$_3$, 25 °C).
Figure S23 $^1$H NMR spectrum of compound 12 (400 MHz, CDCl$_3$, 25 °C).

Figure S24 $^{13}$C APT NMR spectrum of compound 9 (100 MHz, CDCl$_3$, 25 °C).
## 2. Crystallography

Crystallographic data for compounds 1, 9 and 10.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>9</th>
<th>10</th>
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<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₃₄H₃₃N₃O₂·CH₂Cl₂</td>
<td>C₈H₂₇O₃</td>
<td>C₉H₄I₂O₂</td>
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<tr>
<td><strong>M</strong></td>
<td>600.56</td>
<td>399.90</td>
<td>397.92</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2₁/c</td>
<td>C2/c</td>
<td>Pna₂₁</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>6.3450(4)</td>
<td>14.2392(4)</td>
<td>13.6640(3)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>18.5390(17)</td>
<td>7.7434(7)</td>
<td>14.5729(7)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>26.3671(19)</td>
<td>10.2940(3)</td>
<td>4.9121(13)</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>100.026(6)</td>
<td>123.001(3)</td>
<td>4.9121(13)</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>3054.2(4)</td>
<td>951.89(10)</td>
<td>978.1(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td><strong>Dc (g·cm⁻³)</strong></td>
<td>1.306</td>
<td>2.790</td>
<td>2.702</td>
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<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.27 x 0.23 x 0.18</td>
<td>0.22 x 0.21 x 0.09</td>
<td>0.40 x 0.18 x 0.16</td>
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<tr>
<td><strong>μ (mm⁻¹)</strong></td>
<td>0.249</td>
<td>6.577</td>
<td>6.392</td>
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<td><strong>F (000)</strong></td>
<td>1264</td>
<td>720</td>
<td>720</td>
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<tr>
<td><strong>h; k; l range</strong></td>
<td>-7, 7; -23, 23; -32, -18, 18; -10, 9; -13, -16, 17; -18, 18; -6, -6, 6</td>
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<tr>
<td><strong>θ range (°)</strong></td>
<td>1.35; 26.28</td>
<td>3.14; 27.50</td>
<td>2.98; 27.48</td>
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<tr>
<td><strong>Reflections</strong></td>
<td>21298</td>
<td>4414</td>
<td>7810</td>
</tr>
<tr>
<td><strong>measured</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>- independent</strong></td>
<td>21255 (0.0360)</td>
<td>4379 (0.0417)</td>
<td>7790 (0.0408)</td>
</tr>
<tr>
<td><strong>(R_{int})^a)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>- observed [I&gt;2σ(I)]</strong></td>
<td>4426</td>
<td>1027</td>
<td>2137</td>
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<tr>
<td><strong>Parameters refined</strong></td>
<td>379</td>
<td>60</td>
<td>118</td>
</tr>
<tr>
<td><strong>Max / min Δρ (e·Å⁻³)</strong></td>
<td>0.741 / -0.848</td>
<td>1.725 / -1.658</td>
<td>0.499 / -1.405</td>
</tr>
<tr>
<td><strong>GOF^b)</strong></td>
<td>1.092</td>
<td>1.136</td>
<td>1.090</td>
</tr>
<tr>
<td><strong>R(F)^c)</strong></td>
<td>0.0784 / 0.2091</td>
<td>0.0320 / 0.0833</td>
<td>0.0222 / 0.0567</td>
</tr>
</tbody>
</table>

^a) R_{int} = \sum |F_o^2 - F_{o,mean}^2|/\sum F_o^2,  
^b) GOF = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffs} - N_{params})]^{1/2} for all data,  
^c) R(F) = \sum |F_o| - |F_c|/\sum |F_o| for observed data,  
  wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2} for all data.
The X-ray data for single crystals of 1, 9 and 10 were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073Å), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN. The absorption was corrected by integration methods. Structures were solved by direct methods (Sir92) and refined by full matrix least-square based on F² (SHELXL97). Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors H_{iso}(H) = 1.2 U_{eq}(pivot atom) or of 1.5U_{eq} for the methyl moiety with C-H = 0.96, 0.97 and 0.93 Å for methyl, methylene, and hydrogen atoms in aromatic ring, respectively.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 943001, 943002 and 943003 for 1, 9 and 10, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).
Figure S25 The molecular structure (ORTEP 50% probability level) of 1, molecule of CH$_2$Cl$_2$ is omitted for clarity. Selected interatomic distances [Å] and angle [°]: O1 C2 1.215(4), O2 C9 1.218(4), C1 C2 1.479(5), C2 C3 1.508(4), C3 C4 1.394(5), C3 C8 1.405(4), C4 C5 1.403(4), C5 C6 1.387(5), C6 C7 1.393(5), C7 C8 1.398(4), C8 C9 1.500(5); C2 C1 C9 107.8(3).

Figure S26 The molecular structure (ORTEP 50% probability level) of 9. Selected interatomic distances [Å] and angle [°]: I1 C3 2.086(4), O1 C1 1.389(5), O2 C1 1.174(6), C1 C2 1.490(6), C2 C3 1.379(6), C3 C4 1.401(6), C2 C2a 1.399(7), C4 C4a 1.399(9); C1 O1 C1a 111.6(5).
Figure S27 The molecular structure (ORTEP 50% probability level) of 10. Selected interatomic distances [Å] and angle [°]: I1 C4 2.087(4), I2 C7 2.087(4), O1 C2 1.195(6), O2 C9 1.199(6), C1 C2 1.517(6), C2 C3 1.501(5), C3 C4 1.387(6), C3 C8 1.407(6), C4 C5 1.388(6), C5 C6 1.403(7), C6 C7 1.379(7), C7 C8 1.391(5), C8 C9 1.498(6), C9 C1 1.519(6); C2 C1 C9 105.3(3).

Figure S28 Crystal packing of 9 (type A) and 10 (type B) view along axis b
3. HOMO and LUMO localizations

The following figures have been derived from calculations using PM7 method implemented MOPAC2012. The visualizations have been performed in OPchem.

Figure S29 HOMO (red) and LUMO (blue) localizations in chromophore 1.

Figure S30 HOMO (red) and LUMO (blue) localizations in chromophore 2.
Figure S31 HOMO (red) and LUMO (blue) localizations in chromophore 3.

Figure S32 HOMO (red) and LUMO (blue) localizations in chromophore 4.
Figure S33 HOMO (red) and LUMO (blue) localizations in chromophore 5

Figure S34 HOMO (red) and LUMO (blue) localizations in chromophore 6.
Figure S35 HOMO (red) and LUMO (blue) localizations in chromophore 7.

Figure S36 HOMO (red) and LUMO (blue) localizations in chromophore 8.
4. UV-Vis absorption spectra

The following spectra were measured in CH\textsubscript{2}Cl\textsubscript{2} at concentration 1×10\textsuperscript{-5} M.

![Graph of UV-Vis absorption spectrum of compound 1](image1)

**Figure 37** UV-Vis absorption spectrum of compound 1 as a dependence of ε [mol\textsuperscript{-1}dm\textsuperscript{3}cm\textsuperscript{-1}] on λ [nm].

![Graph of UV-Vis absorption spectrum of compound 2](image2)

**Figure 38** UV-Vis absorption spectrum of compound 2 as a dependence of ε [mol\textsuperscript{-1}dm\textsuperscript{3}cm\textsuperscript{-1}] on λ [nm].
Figure 39 UV-Vis absorption spectrum of compound 3 as a dependence of \( \varepsilon \) [mol\(^{-1}\)dm\(^3\)cm\(^{-1}\)] on \( \lambda \) [nm].

Figure 40 UV-Vis absorption spectrum of compound 4 as a dependence of \( \varepsilon \) [mol\(^{-1}\)dm\(^3\)cm\(^{-1}\)] on \( \lambda \) [nm].
**Figure 41** UV-Vis absorption spectrum of compound 5 as a dependence of $\varepsilon$ [mol$^{-1}$dm$^3$cm$^{-1}$] on $\lambda$ [nm].

**Figure 42** UV-Vis absorption spectrum of compound 6 as a dependence of $\varepsilon$ [mol$^{-1}$dm$^3$cm$^{-1}$] on $\lambda$ [nm].
Figure 43 UV-Vis absorption spectrum of compound 7 as a dependence of $\varepsilon$ [mol$^{-1}$dm$^3$cm$^{-1}$] on $\lambda$ [nm].

Figure 44 UV-Vis absorption spectrum of compound 8 as a dependence of $\varepsilon$ [mol$^{-1}$dm$^3$cm$^{-1}$] on $\lambda$ [nm].
Figure 45 UV-Vis absorption spectrum of compound 11 as a dependence of $\varepsilon$ [mol$^{-1}$dm$^3$cm$^{-1}$] on $\lambda$ [nm].

Figure 46 UV-Vis absorption spectrum of compound 12 as a dependence of $\varepsilon$ [mol$^{-1}$dm$^3$cm$^{-1}$] on $\lambda$ [nm].
5. References


4. SHELXL-97, Sheldrick, G. M., University of Göttingen, Göttingen, **2008**.
